Testing of Fuels in Fuel Cell Reformers

2003 Hydrogen and Fuel Cells Merit Review Meeting

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FY2003: Funding: $1200k (Program Manager Nancy Garland)

divided between:

Fuels (Gasoline Component) Testing - (FY2002 $300k)

Gasoline Reformate and H_2 PEM Durability

Diesel Reforming (SECA program)

Technical Objectives:

Examine Fuel Effects on Fuel Processor Performance and Durability

- Quantify fuel effects on performance and durability.
    - Fuel component, impurity, additive effects
- Examine fuel effects on fuel processor start-up
- Understand parameters that affect fuel processor and stack lifetime and durability.
    - Fuel processor catalyst stability and activity
    - Evaluate fuel effect and start-up effect on carbon formation
    - Identify chemical species limiting durability
    - Durability testing to evaluate long term performance

- Fuel Processor (& System) Targets:

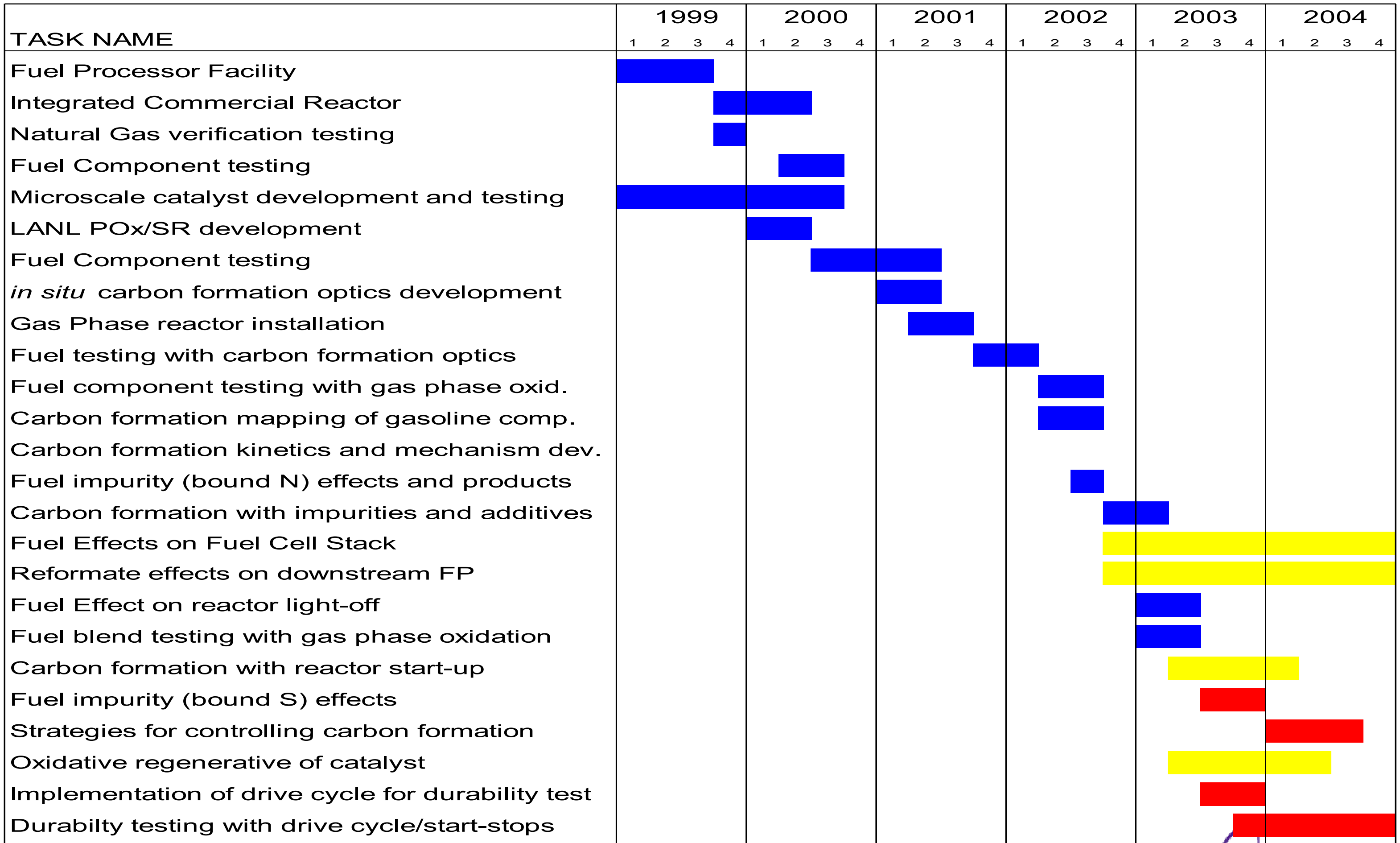
• Power density, specific power, cost		(catalyst performance and loading)
• Cycle capability		(light-off, durability testing)
• Start-up Time	(Barrier I)	(light-off temperature and performance)
• Energy efficiency	(Barrier M)	(fuel performance)

- Fuel Processor Barriers:

• Durability.	(Barrier J)	(durability and carbon formation studies)
• Fuel Pr. Start-up/Transient		(fuel effect on light-off)
• Cost.	(Barrier N)	(effect on catalyst loading and durability)

Fuels Testing Timeline

Project initiated in 1999 / Fuels testing initiated 2000
Part of Multi-year-program-plan Fuels for Fuel Cells (5 yr) program



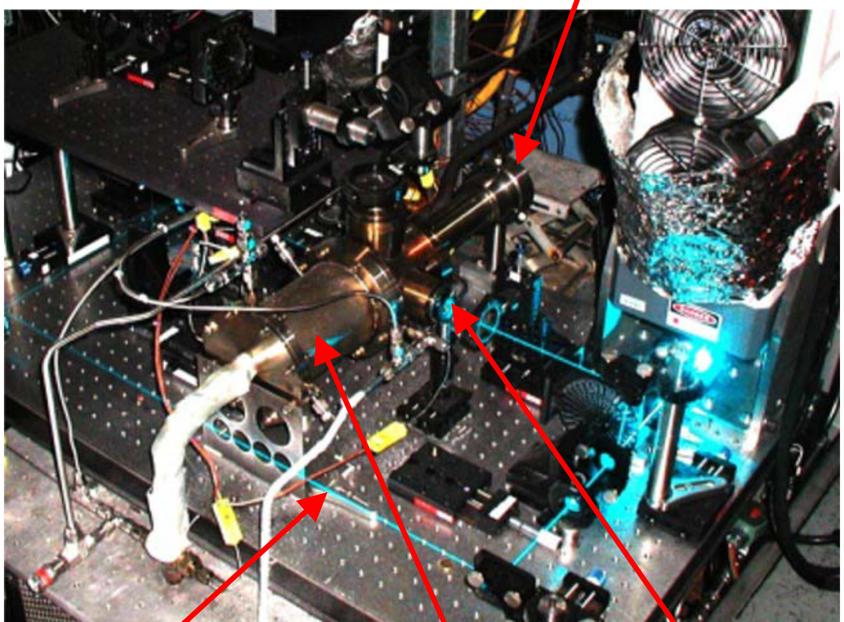
Approach to Fuels Testing

- Measure fuels effects in fuel reformers
  - Adiabatic, vehicle scale reformers
    - Catalytic partial oxidation / steam reforming
    - Gas phase partial oxidation / catalytic steam reforming
- Fuel reforming kinetics
  - Ease of partial oxidation / steam reforming
    - Fuel components, fuel impurities, fuel additives
  - Effect on light-off (fuel processor start-up)
- Measure Carbon formation
  - Fuel effect on steady state, startup and transient carbon formation
- Effect on fuel processor durability
  - Measure carbon formation
  - Hydrocarbon breakthrough

Adiabatic Reactor Testing / ‘Vehicle’ Scale

Catalytic
Partial Oxidation/Steam Reforming
in situ Carbon Formation Laser Optics

Reactor Window

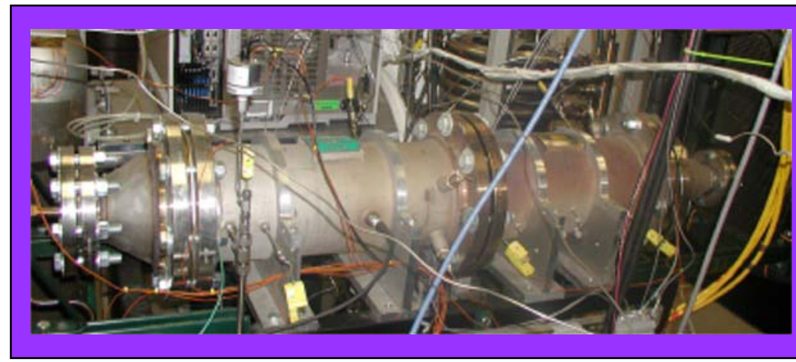


Reference Beam

Reactor

Reactor Window

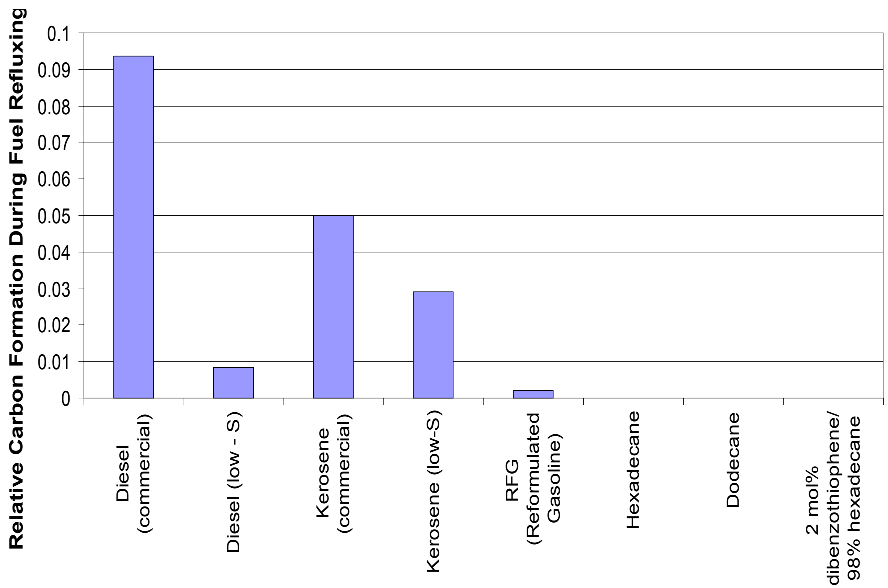
Gas phase partial oxidation



Fuel components testing with gas phase partial oxidation / catalytic steam reforming

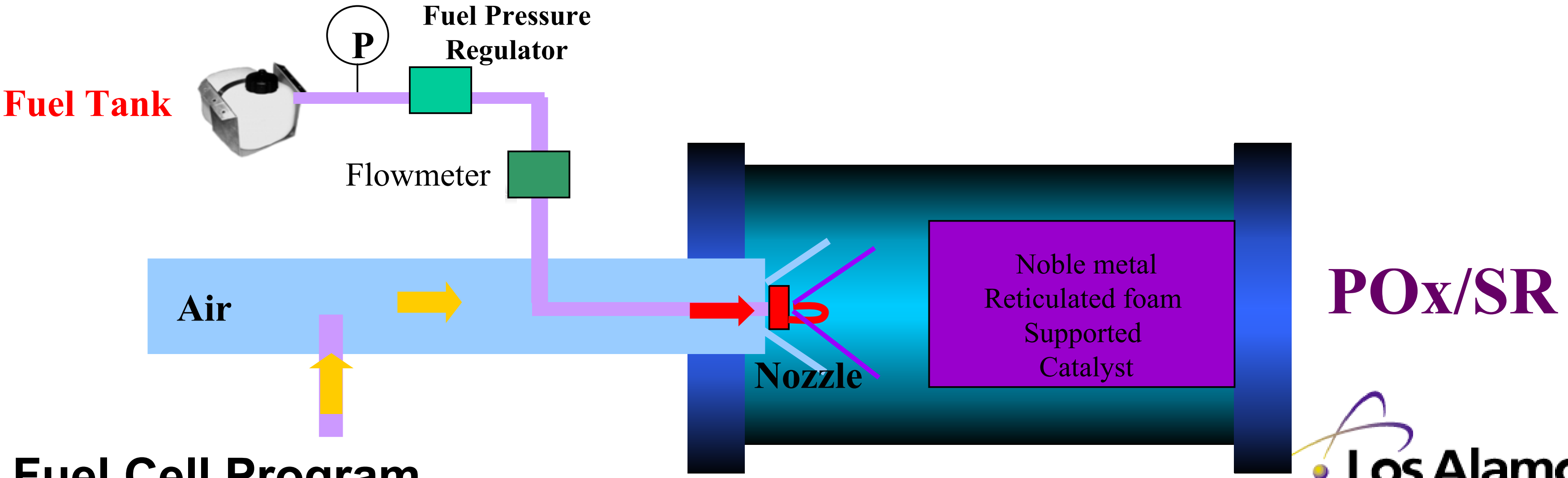
(provided by Nuvera)

Relative Carbon Formation from Fuel Vaporization

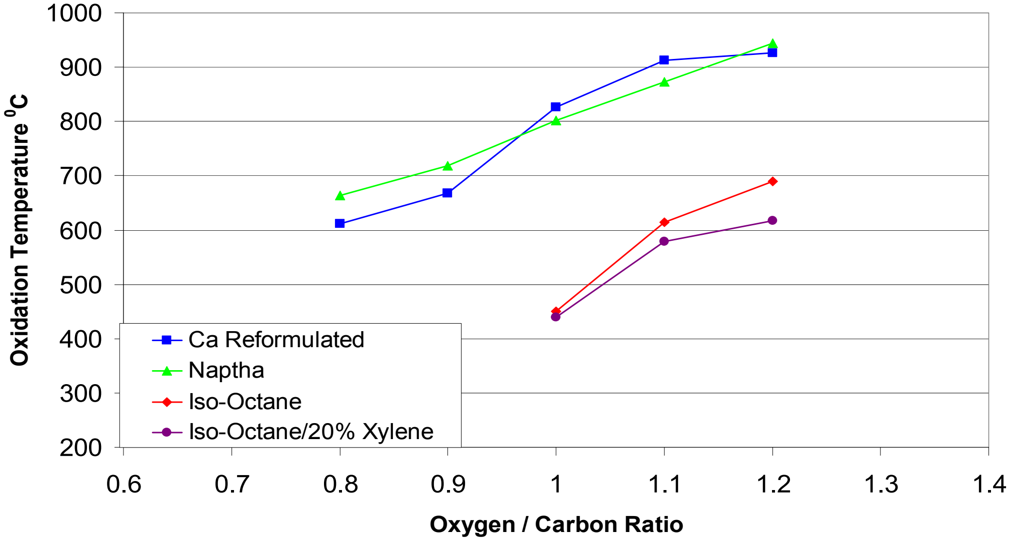


Diesel fuel shows pyrolysis upon vaporization

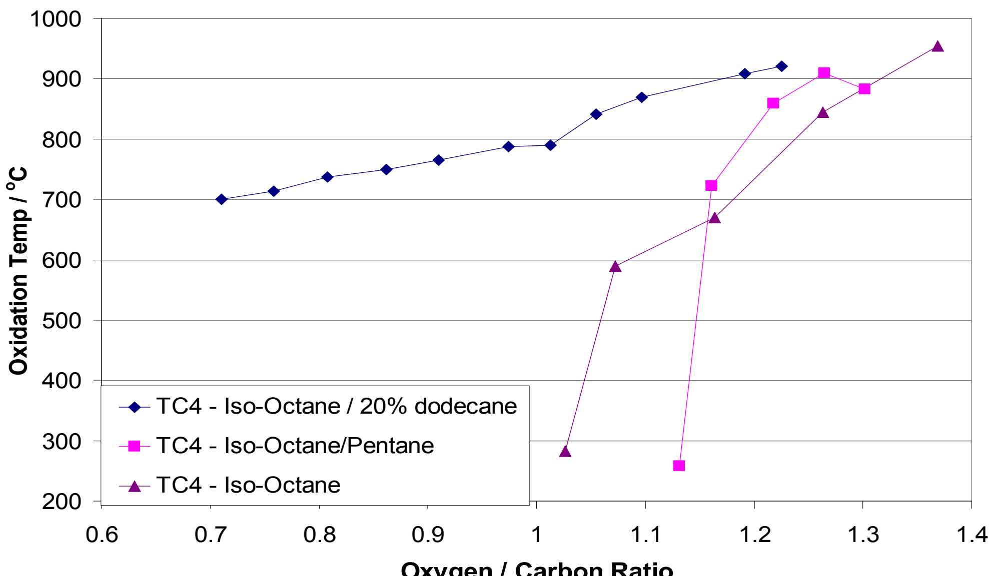
- Diesel fuel reformers require
  - Direct fuel injection
  - Water to suppress carbon formation
- Directly inject fuel to reforming catalyst
  - Commercial fuel nozzle
  - Limited preheating of fuel/air
    - Prevents fuel vaporization/particulate formation
  - Carbon formation experiments under real conditions



Fuels During Gas Phase Oxidation



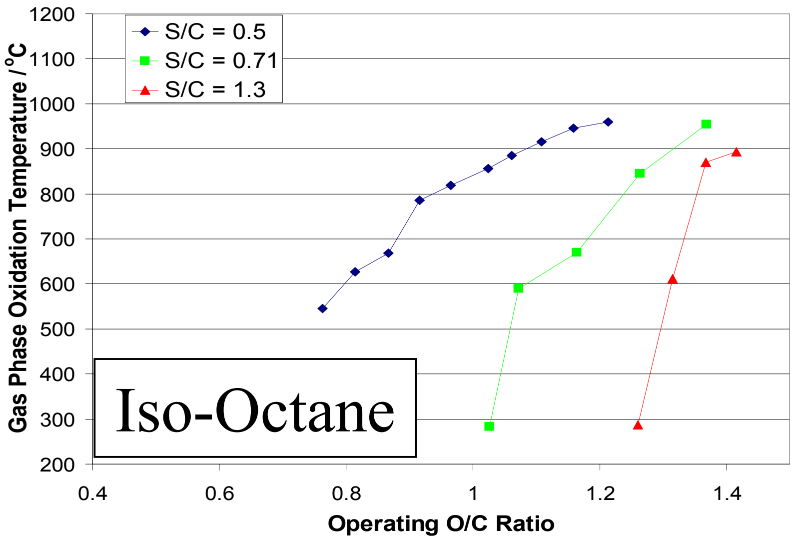
- Gas phase oxidation was easier with ‘real’ fuels
- Difficult to keep combustion with pure components iso-octane and iso-octane/xylene

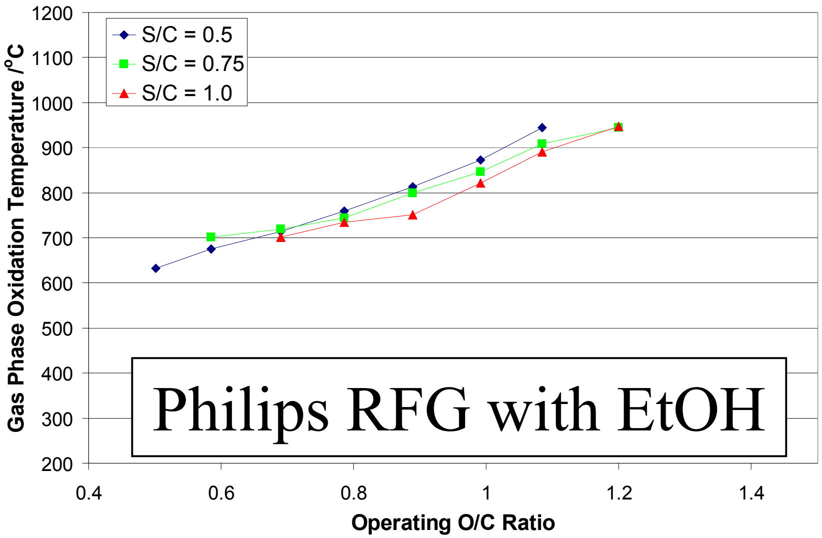


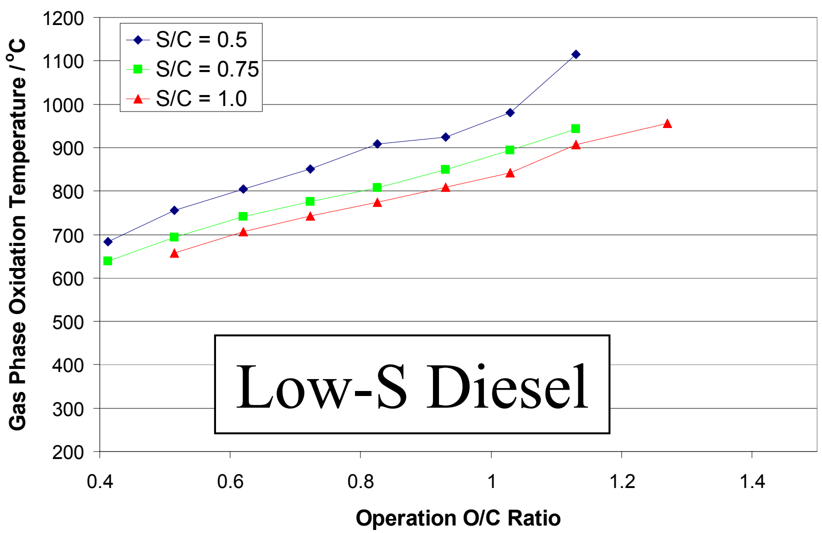
- Adding dodecane to iso-octane simulated oxidation of fuel blends.
- Addition of pentane shows essentially same results as iso-octane.
- Addition of heavier hydrocarbons provides easier gas phase oxidation

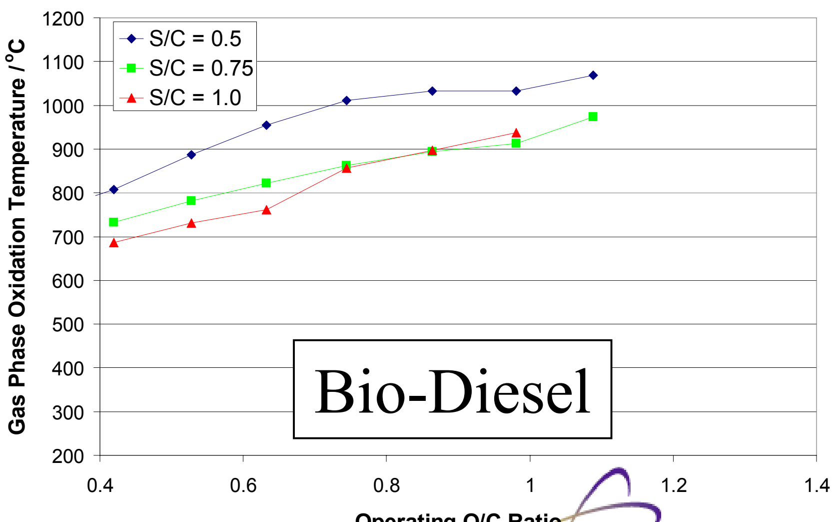
Gas Phase Partial Oxidation of Fuels

Steam/carbon effect on fuel oxidation

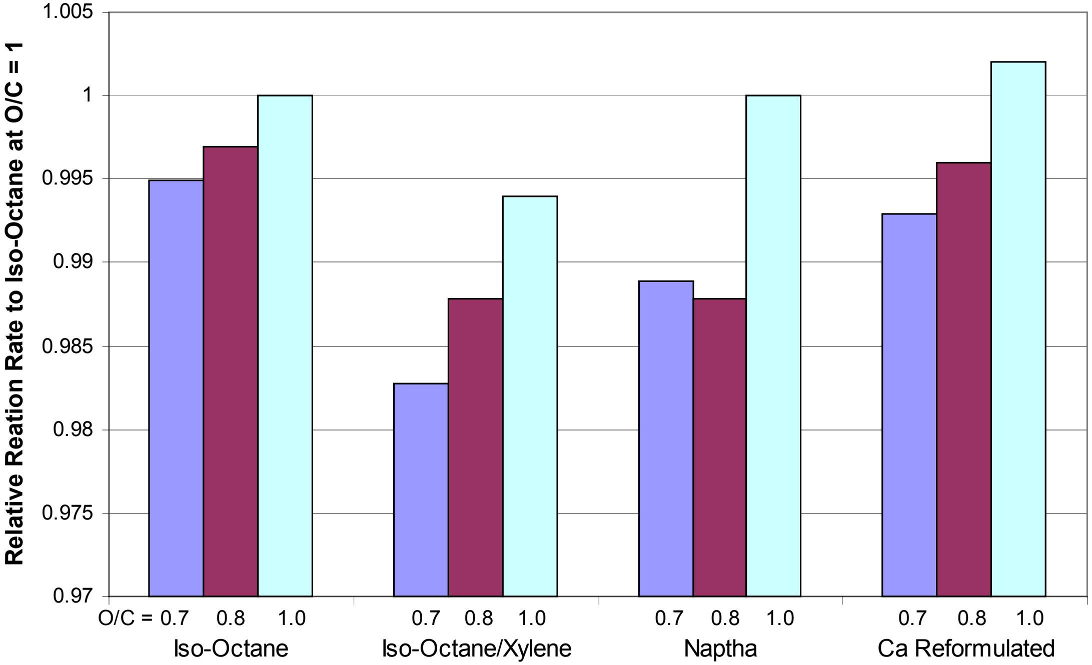








Catalytic Partial Oxidation Stage



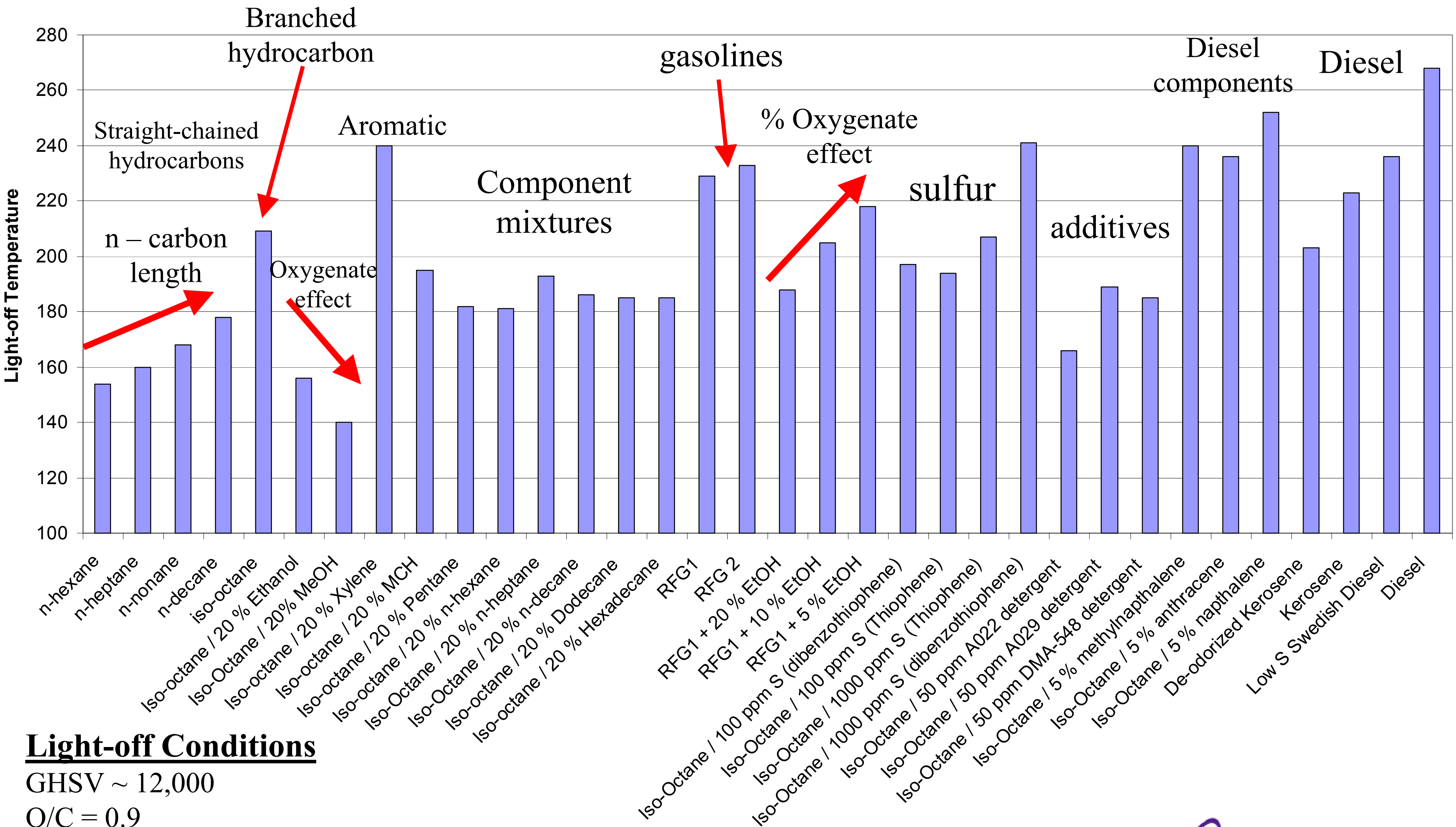
Aromatics slow oxidation and reforming

Longer Chained hydrocarbons also slow reforming kinetics

Higher Temperatures (O/C ratio's) are required for long chained hydrocarbon conversion for similar residence times – leads to H_2 dilution

- **For full conversion of hydrocarbon fuels which include long chains, aromatic:**
  - **Either longer residence times required for similar conversion**
    - **leads to bigger reactor, more catalyst**
  - **Higher Temperature → O/C, which leads to inefficiency**

Fuel Effect on Catalyst Light-off



<u>Light-off Conditions</u>

GHSV ~ 12,000

O/C = 0.9

S/C = 1.0

Fuel Effect on Reactor Light-off

Fuel Effect on Gas Phase Reactor Light-off

Reactor light-off (ignition) can vary with fuel and fuel components:

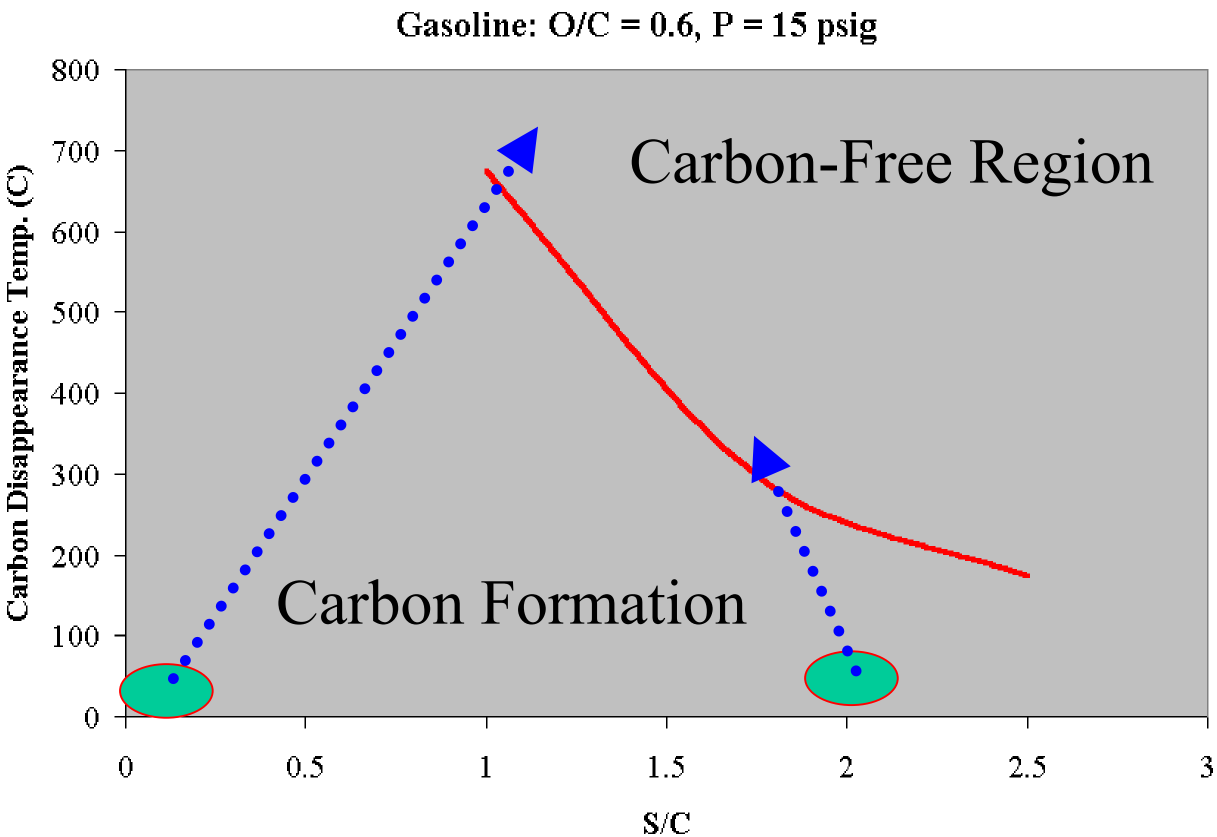
For Gas Phase oxidation reactor ignition requires:

Iso-Octane:	O/C = 1.2, at S/C ~ 0.5
RFG (gasoline):	O/C = 1.0, at S/C ~ 0.5

Fuel Effect on Catalytic Reactor Light-off

- Fuel Composition Effects on fuel processor operation
  - Gas phase oxidation prefer high long-chained hydrocarbons
  - Catalyst oxidation prefer shorter chained hydrocarbons
- Light-off
  - oxygenated compounds speed light-off
  - straight-chained hydrocarbons ease light-off compared with branched
  - aromatics slow kinetic light-off
  - long chained hydrocarbons (diesel) slow light-off
- Light-off Temp. corresponds inversely to C-H or C-C Bond dissociation energy

Equilibrium Modeling



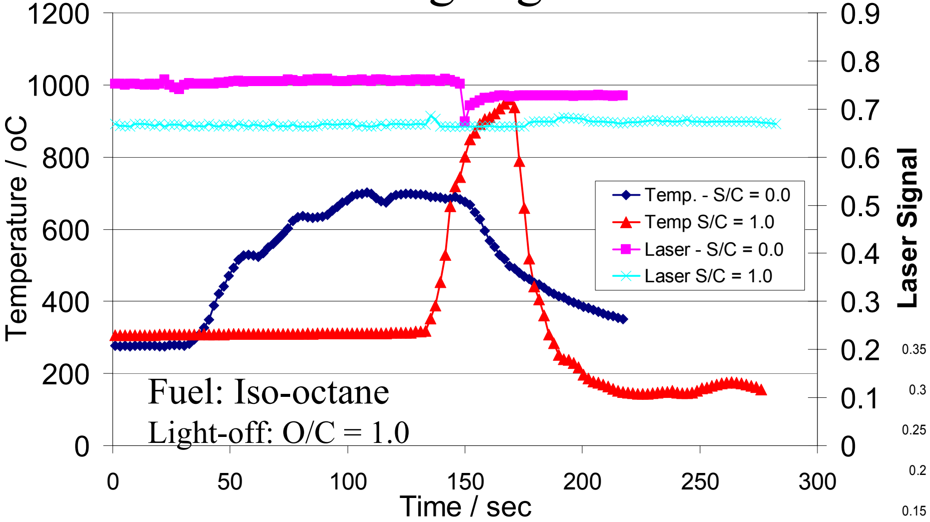
Equilibrium defines fuel processor operating conditions

At start-up of fuel processor, water availability is questionable (freezing conditions)

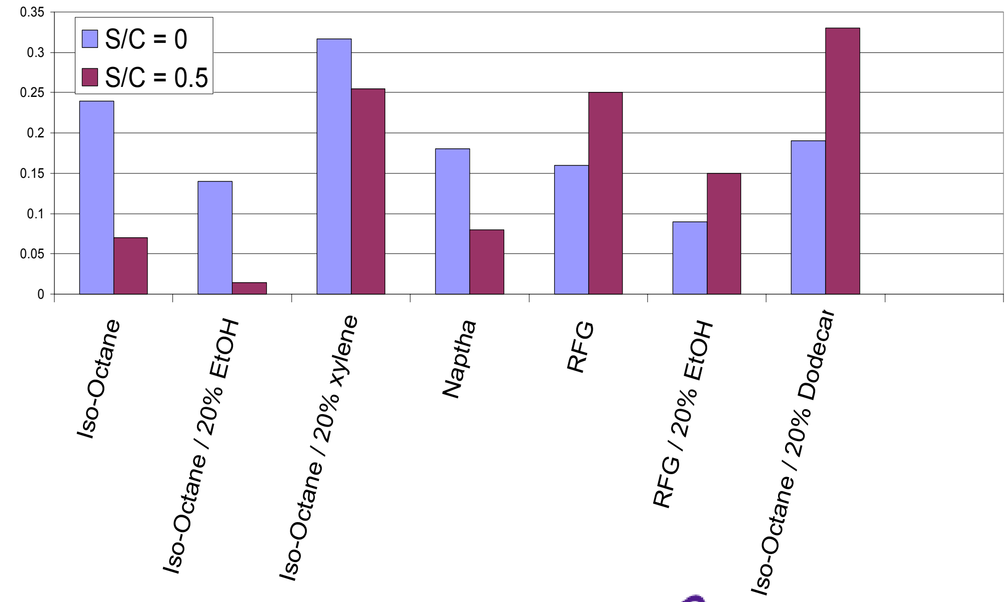
Avoiding zero equilibrium carbon will be difficult whether water is available or not.

At high S/C during start-up, during transition to carbon-free region - carbon formation kinetics appear low

Carbon formation during reactor light-off



In situ laser measurement during light-off of fuel conducted at S/C = 0.0, and S/C = 0.5 for fuels including iso-octane, iso-octane/xylene, iso-octane/ethanol, iso-octane/dodecane, naptha, reformulated gasolines (RFG), RFG/ethanol, Iso-octane /dodecane and Iso-octane/pentane.



Quantitative carbon measurements indicate carbon made during start-up for all fuels. Water during start-up suppresses some carbon formation, but carbon is still formed, in smaller quantities.
Ethanol suppresses carbon formation, while aromatics shower high carbon formation.

Carbon Formation Effect on Durability

- Carbon formation during operation and start-up
  - function of fuel composition, also O/C and S/C

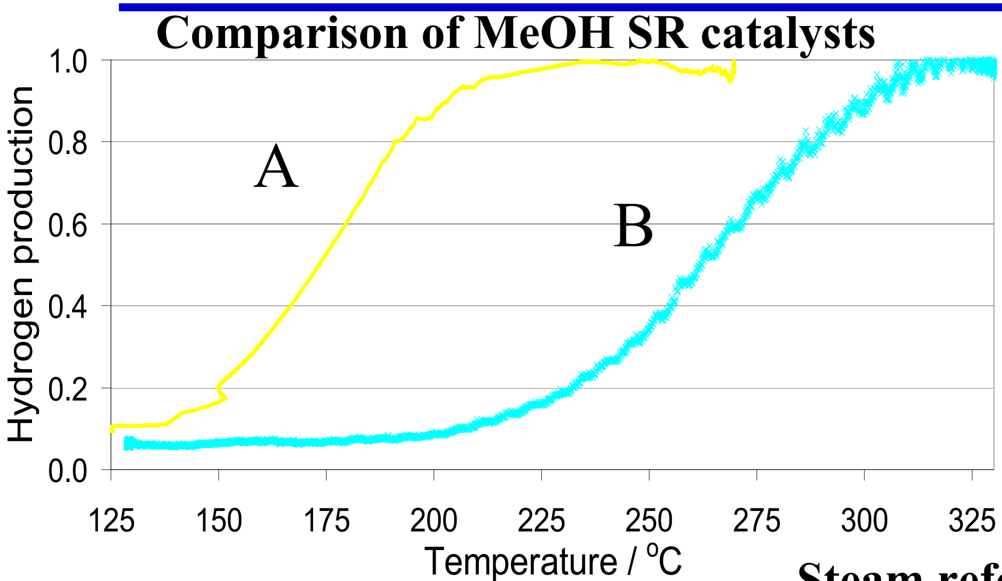
- Carbon formed during start-up ~ 0.5 % to 3 % of carbon from fuel (for 30 sec)
- Normal operation at O/C = 0.75, S/C => 1.0, no measurable carbon

- Ethanol addition decreases carbon formation: 40 % (RFG) to 80% (Iso-Octane)

- Durability targets 5000 hrs. (# start-ups 4,000 – 10,000 cycles (drive cycle))
  - RFG (4,000 cycles) forms 1.0 kg carbon
  - RFG (10,000 cycles) forms 2.5 kg carbon

- Post-catalyst analysis does not show carbon poisoning noble metal catalysts
  - carbon typically moves down stream in system
- Carbon formation with nickel catalyst tends to remain in ATR

Low Temperature Reforming Fuels
Support of portable power



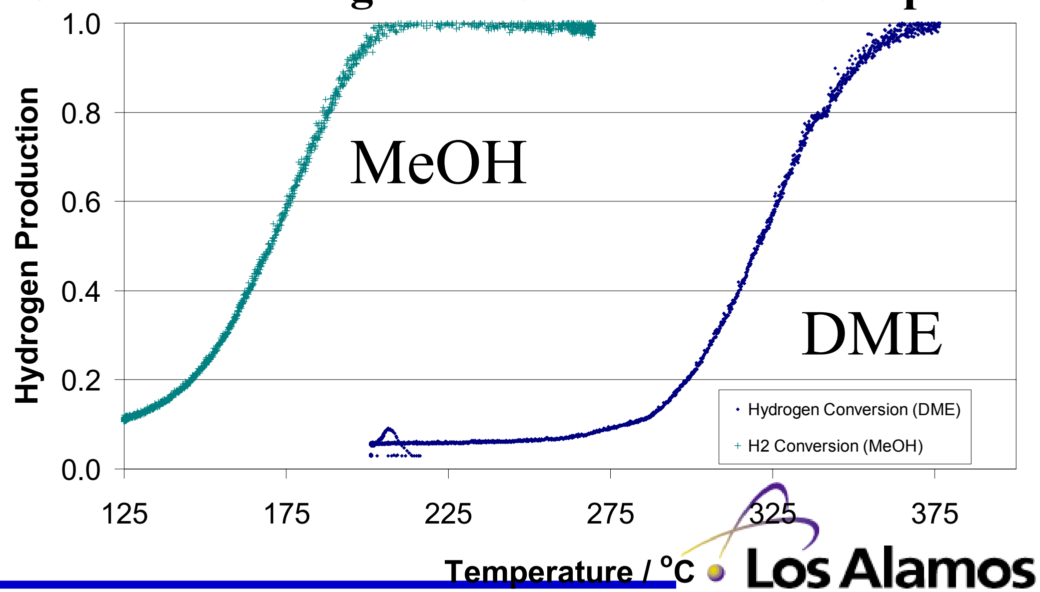
MeOH (Methanol)
H_2O/MeOH = 1.5
Space Time = 0.5 sec

DME (DiMethylEther)
S/C = 2.5
Space Time = 0.5 sec

Full conversion of MeOH at ~ 200 – 220 °C (~ 10,000 GHSV)

TON at ~ 220 °C 8.5 per min
(based on CO adsorption sites)

Full conversion of DME at 360 – 380 °C



2002 Fuel Cell Review Comments

–Not clear that results show ‘durability’ – instead appear to provide valuable insight into transient response. Can effect of shut-down overshadow long-term ‘normal’ ATR Operation?

Believe that the short term effects are durability effects – these ‘transient’ effects can be significant during start-up, shut-down and potentially overshadow long-term operation.

– Unclear how iso-octane can provide knowledge addressing durability issues – why is ‘normal’ gasoline not used for tests?

– Important to address issues of effect of normal gasoline on whole system

– Use ‘real’ reformate & publish results

We are using various components, including gasoline

– In-situ method is an excellent approach – however work presented appears to provide durability during transient behavior, not necessarily long-term operation.

We use in situ measurements define short term fuel effects to extrapolate to durability. We also do long-term operation to define durability. Durability system operates with adiabatic reactor, with HTS/LTS, PrOx and slip stream to PEM cells. Hydrocarbon breakthrough in ATR limits durability

Interactions/Collaborations

- National Technical Presentations/Publications
  - AIChE, ACS, SAE
- Delphi Automotive
  - discussions (~ reactor design, testing, diesel)
- CRADA Interactions
  - Motorola (MeOH SR)
- Haynes International (reformer materials)
- Phillips Petroleum
  - providing fuel for testing, additives, fuel formulations
- Catalysts (for fuel reforming (gasoline, diesel, MeOH), Durability)
  - Univ. Alabama, Engelhard, Delphi, Süd-Chemie, Johnson Matthey

2002 - 2003 Milestones

	Gasoline
May 2002	500 - 1000 hrs of operation durability in adiabatic reactor
September 2002	Carbon formation with detergent additives
June 2003	Comparison Measurements of carbon formation effect at start-up and light-off for 4 fuel components and 2 fuel
September 2003	Measurement of sulfur effect on carbon formation
	Methanol
December 2002	Relative reaction rate evaluation of 4 existing methanol steam reforming catalysts
July 2003	Kinetic rate expression development for Methanol steam reforming catalyst
	Diesel (SECA Program)
December 2002	Direct Fuel Injection/Air Mixing Demonstration
March 2003	Multiple Regeneration Cycles Removing Carbon From Catalytic Partial Oxidation
September 2003	Carbon Formation Kinetics Rate Expression Development

Summary/Findings

- ATR of Fuel Components
  - Catalytic vs. gas-phase
    - gas-phase oxidation favors 'real' fuel mixtures and higher hydrocarbons
      - Steam input has large effect on gas phase oxidation, small on catalytic
    - Catalytic oxidation favors short-chained aliphatic hydrocarbons
      - Aromatics/long-chained HC's have lower catalytic kinetics
- Fuel Effect on Reactor Light-off
  - Homogeneous
    - high steam content slows light-off
  - Catalytic
    - oxygenated, straight-chained HCs speed light-off
    - aromatics, branched chained slow light-off
- Carbon Formation
  - Monitoring carbon formation during the start-up transient
    - Aromatics show highest tendency for carbon formation
    - Oxygenates help suppress carbon formation during light-off

Future Plans

- Remainder of FY 2003:
  - Carbon formation:
    - Sulfur effect on carbon formation
    - Oxidative regenerative of catalyst
  - Fuel reforming and hydrogen fuel cell durability testing
    - Implement drive cycle testing into durability testing
- FY 2004:
  - Hydrogen / gasoline reformate durability comparison
    - Implementation of drive cycle including start-up cycling on fuel processor
  - Carbon formation fundamentals
    - Kinetic expressions and mechanistic studies of carbon formation
  - Strategies for controlling carbon formation
    - Avoidance and minimization of carbon formation
    - Oxidative regeneration of catalyst
  - Characterization of start-up emissions
    - Contaminant and hydrocarbon breakthrough